The first Moscow Solar System Symposium (1M-S^3)
Mars system studies
Moscow 2010

PLANETARY LASER RAMAN SPECTROSCOPY FOR SURFACE EXPLORATION ON PHOBOS and DEIMOS -- A FEASIBILITY STUDY.

Alian Wang[1], W. G. Kong[1,2], [1]*Dept Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO, 63130 USA (alianw@levee.wustl.edu),* [2] *School of Space Science and Physics, Shandong University, Weihai, 264200, China.*

Introduction: C/D-type asteroids occur in the outer part of main asteroid belt of our solar system. Missions to asteroids that have flown or will fly include the flybys (Voyager, Deep Space 1, Galileo by NASA, Rosetta by ESA), orbiters (NEAR Shoemaker and Dawn by NASA), lander (NEAR Shoemaker by NASA), and sample return (Hayabusa by JSA, Phobos Grunt by Russia, Marco Polo by ESA-JSA). Asteroids have been selected as the exploration targets because they were recognized to contain primitive materials from the early development stages of our solar system.

In situ characterizations of surface and subsurface materials of asteroids are important to understand the evolution of the early solar system, the asteroids them-selves, and their contributions to the planetary bodies of inner solar system [1]. This task can be achieved by Planetary Laser Raman Spectroscopy.

Planetary Laser Raman spectroscopy: When irradiated by a laser beam, a molecule may absorb a photon and instantly emit a new photon with the same wavelength (Rayleigh scattering) or a different wavelength (Raman scattering). The wavelength of Raman scattering is a function of molecular structure and composition. With a laser excitation line in the visible spectral range, a Raman spectrometer (with optics and a detector optimized for visible radiation) observes the vibrational and rotational transitions of a molecular system, which are normally observed by Near-IR, Mid-IR, and Far-IR spectroscopy.

Minerals and organic functional groups all have unique Raman spectra enabling unambiguous phase identification [2,3,4]. Compared to VIS-NIR and Mid-IR emission or reflectance spectra, Raman peaks are sharp, non-overlapping, and nearly free of overtones and combinations. Minerals and organic species can be readily identified even in raw spectra of mixtures. Spectral patterns and peak positions, not peak intensities, are used for identification. Organic species need not to be crystalline for detection. Raman Peak position and peak width are not affected by grain sizes [5,6].

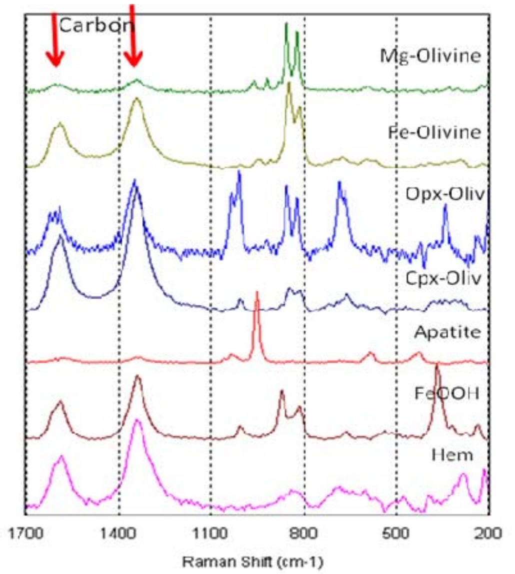
The major Raman peaks of oxy-anionic species (silicates, phosphates, sulfates, carbonates, etc.) are determined by the chemical bonds with the highest covalence in a structure (i.e. SixOy, PO_4, SO_4, CO_3, etc), with peak positions to be modified by cations that link to them [7,8,9,10]. Rapid mineral classification and detailed structural and compositional information can be obtained through laser Raman measurements in robotic surface exploration missions.

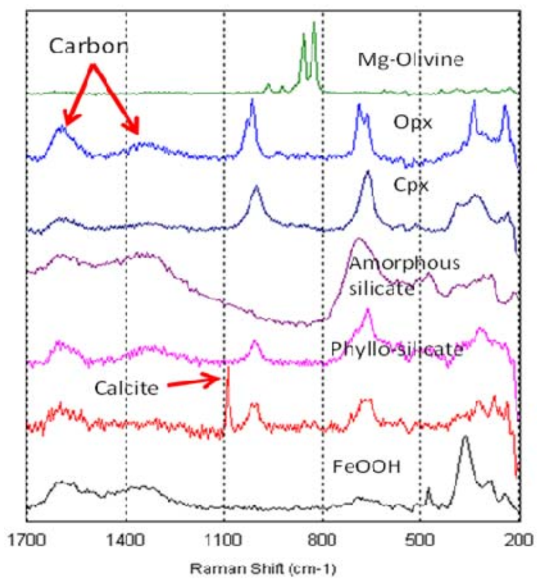
Raman signals can sometimes be covered by competing fluorescent photons. To overcome that interference, a "contact" Raman system uses a highly condensed excitation laser beam (10-20 µm diameter) and a short working distance (~ cm) which will ensure the highest efficiency for Raman signal excitation and collection, permitting a high detection sensitivity for many species [11]. In addition, a narrow excitation laser beam will provide the capability to detect minor or trace species whose signal would be obscured by major species if using a broad beam for excitation. In order to obtain the information on mineral modes and texture information, multiple Raman spectra will be required to be taken from one sample of rocks or regolith at the surface or subsurface of asteroid [12].

A feasibility study: Because carbonaceous chondrites are thought to have a similar origin as C/D-type asteroids (early solar system material), we conducted a Raman spectroscopic study of Murchison and Allende to demonstrate that Planetary Laser Raman Spectroscopy can address the major science questions during a surface exploration mission to Phobos or to Deimos. The Murchison and Allende meteorites are two of the most studied carbonaceous meteorites due to their large mass. Murchison belongs to the CM2 group and was partially altered in its parent body [1]. Allende belongs to CV3 group and has experienced low temperature metamorphism in its parent body [13]. Raman spectroscopy has been used to study the carbonaceous matter in the Murchison meteorite [14, 15].

Samples and measurements: Powdered samples and flat-cut rock chips from each of the Murchison and Allende meteorites were used for this study. A HoloLab5000-532 laser Raman spectrometer (Kaiser Optical Systems Inc.) was used to obtain Raman spectra of 4000 -100 cm^{-1}, that uses a 532 nm frequency-doubled Nd:YAG laser for excitation and a objective lens to condense a ~ 6 um diameter laser beam onto the sample. Automatic linear scans (99% time off-focus with known de-focusing distance) were made on both the powder and rock samples. Two sets of manual scans (100% time at-focus) were made for comparison reason.

Figure 1 and 2 show the typical Raman spectra obtained from major, minor, and trace species in the two meteorites.





Information obtained: 600 Raman spectra were obtained from six traverses of 100 points each, 91-97% of the spectra from each of three traverses on Murchison are informative, and 70-98% of the spectra from each of three traverse on Allende are informative. We found that the major challenge for obtaining an informative Raman spectrum from a measurement on those meteorite samples is not the off-focus distance (maximum ~ 0.1 mm for powder sample) but the fluorescence.

The Raman spectra in Figure 1 and Figure 2 demonstrated that the major, minor and even some trace mineral phases in Murchison and Allende were identified through Raman measurements. Furthermore, using the Raman peak positions of olivine and pyroxene, the Mg/(Mg+Fe) ratio in olivine and Mg/(Mg+Fe+Ca) ratio in pyroxene can be determined, thus we were able to obtain the compositional distributions of olivine and pyroxene in these two meteorites (Figure 3 & Figure 4), which relate directly to their crystallization history. In addition, the Raman carbon peak area ratios (Fig. 1 and Fig. 2) reveal the crystallinity of graphitic carbons in Murchison and Allende which directly link to the different metamorphic grades of these meteorites.

The mineral ID and additional information can also be obtained during the surface exploration on Phobos and Deimos by laser Raman Spectroscopy.

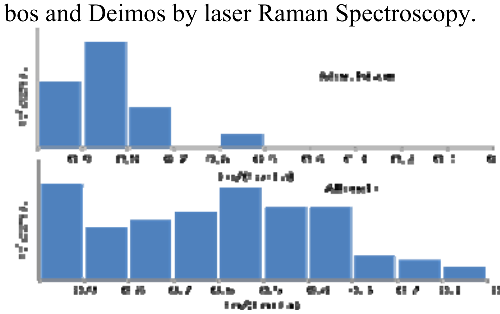


Figure 3: Fo/(Fo+Fa) molar ratio distribution for olivine in Murchison and Allende meteorites.

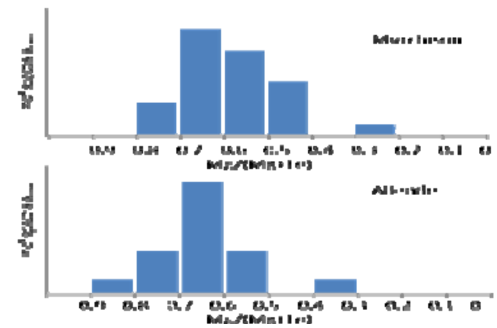


Figure 4: Mg/(Mg+Fe) molar ratio distribution for pyroxene in Murchison and Allende meteorites.

Conclusion: When employed in the surface exploration on Phobos and Deimos, laser Raman spectroscopy will provide the identification of major, minor, and sometimes trace minerals. At the same time, the detailed spectral information will provide compositional distribution of silicates and metamorphic grade of graphitic carbon, which directly link to the formation condition of these asteroids and their evolutional history.

Acknowledgment: W. G. Kong thanks the support of Chinese Scholarship Council for his Ph. D training at Washington University in St. Louis.

References: [1] McSween H. Y. (1979) *GCA* 43, 1761-1770. 2] Nakamoto K. (2009) *Infrared and Raman Spectra of Inorganic and Coordination Compounds, 6th edition.* [3] Wang A. et al. (1994) *Appl. Spectrosc.* 48,959-968. [4] Nyquist R. et al. (1996) *Handbook of Infrared and Raman Spectra of Inorganic Compounds and Organic Salts.* [7] Wang A. et al. (2001) *Am. Mineral. 86,* 790-806; [8] Kuebler et al. (2006) *GCA* 70,6201-6222 [9] Wang A. et al. (2004) *Am. Mineral.* 89, 665-680. [10] Freeman J.J. (2008) *Can. Mineral.* 46, 1477-1500. [11] Wang A. et al. (2003) *JGR* 108, E15005 [12] Haskin et al. (1997) *JGR* 102, 19293-19306 [13] **Weinbruch S. (1994) *GCA* 58, 1019-1030. [14]** Larsen K. L. and Nielsen O. F. (2006) J. *Raman Spectrosc.* 37, 217-222. [15] **Chahrazade E. A. (2005)** *SPECTROCHIM ACTA A* 61, 2049-2056. [16] Wang A. et al. (2004) *J. Raman Spectrosc.* 35, 504-514.